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Reversible, diffusionless, first-order solid-solid phase transitions accompanied by caloric effects are critical for applications in the solid-state cooling and heat-pumping devices. Accelerated discovery of caloric materials requires reliable but faster estimators for predictions and high-throughput screening of system-specific dominant caloric contributions. We assess reliability of the computational methods that provide thermodynamic properties in relevant solid phases at or near a phase transition. We test the methods using the well-studied B2 FeRh alloy as a “fruit fly” in such a materials genome discovery, as it exhibits a metamagnetic transition which generates multicaloric (magneto-, elasto-, and baro-caloric) responses. For lattice entropy contributions, we find that the commonly-used linear-response and small-displacement phonon methods are invalid near instabilities that arise from the anharmonicity of atomic potentials, and we offer a more reliable and precise method for calculating lattice entropy at a fixed temperature. Then, we apply a set of reliable methods and estimators to the metamagnetic transition in FeRh (predicted 346 ± 12 K, observed 353 ± 1 K) and calculate the associated caloric properties, such as isothermal entropy and isentropic temperature changes.

Keywords

caloric, Thermodynamic, Metamagnetic, Phase transformation, FeRh

Disciplines

Materials Science and Engineering

Reliable thermodynamic estimators for screening caloric materials

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Abstract

Reversible, diffusionless, first-order solid-solid phase transitions accompanied by caloric effects are critical for applications in the solid-state cooling and heat-pumping devices. Accelerated discovery of caloric materials requires reliable but faster estimators for predictions and high-throughput screening of system-specific dominant caloric contributions. We assess reliability of the computational methods that provide thermodynamic properties in relevant solid phases at or near a phase transition. We test the methods using the well-studied B2 FeRh alloy as a “fruit fly” in such a materials genome discovery, as it exhibits a metamagnetic transition which generates multicaloric (magneto-, elasto-, and baro-caloric) responses. For lattice entropy contributions, we find that the commonly-used linear-response and small-displacement phonon methods are invalid near instabilities that arise from the anharmonicity of atomic potentials, and we offer a more reliable and precise method for calculating lattice entropy at a fixed temperature. Then, we apply a set of reliable methods and estimators to the metamagnetic transition in FeRh (predicted 346 ± 12 K, observed 353 ± 1 K) and calculate the associated caloric properties, such as isothermal entropy and isentropic temperature changes.

Keywords: caloric, thermodynamic, metamagnetic, phase transformation, FeRh.

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1. Introduction

Solid-state caloric devices have a potential to save vast amounts of electricity [1, 2, 3, 4, 5, 6]. However, predicting thermodynamics in a caloric material can be challenging [7], as near the phase transformation – where caloric effects are induced – the system is on the edge of stability, often with multiple instabilities competing. Hence, thermodynamic estimators need a serious assessment before applications to caloric systems [8], or for use in high-throughput screening supplemented using databases and machine-learning techniques.

The caloric effect is typically quantified by the isothermal entropy change ΔS_T and associated isentropic temperature change ΔT_S at the phase transition at a critical temperature T_c . But these are not the only important quantities. Others include the enthalpy change ΔH at a fixed pressure P or temperature T (importantly, $\Delta H_P \neq \Delta H_T$), the hysteresis width, dependences of T_c on composition and external fields, etc. Thus, a search for a good caloric material involves simultaneous optimization of multiple parameters. For their accurate prediction, it is important to take into account several contributing physical effects, using multi-physics, multi-parameter modeling. On the other hand, quick estimates of the lower and upper bounds allow fast rejection, needed for the high-throughput materials screening.

Our key goal here is to test the reliability of various (often commonly used) methods and to validate our results with those that are measured. The overarching need is a set of reliable, and preferably fast, estimators for thermodynamic quantities for screening, especially for desired outliers – say, materials with a large caloric response. Such materials, however, have electronic (including magnetic) and structural instabilities, in which case the vibrational contributions are often not harmonic; and yet quasiharmonic phonon methods are commonly used.

To analyze and test methods and estimates, we use the multicaloric FeRh system. With its chemical simplicity and well-studied metamagnetic transition, FeRh serves as a wonderful “fruit fly”, or test system, in the materials genome discovery of better caloric systems [9]. However, a long-studied material is not necessarily well understood; there is a continued controversy among the directly measured and indirectly assessed experimental data, as we discuss.

Interestingly, FeRh [10, 11, 12, 13, 14] and NiTi austenite [15, 16, 17, 18] have the same nominal chemical B2 structure (CsCl, $Pm\bar{3}m$ space group, see Fig. 1) and exhibit a large caloric effect [19, 20, 21, 22, 23, 24]. Both B2 austenites (FeRh below 353 K and NiTi above 313 K) have a premartensitic instability with known unstable phonon modes [16, 17]. While they both show elasto- and baro-caloric responses, FeRh also exhibits a giant magnetocaloric effect at its metamagnetic

	Theory	Expt.	Units	Ref.
M (FM)	149	≈ 150	$\text{A m}^2 \text{kg}^{-1}$	[42]
a (FM)	3.012	2.997	\AA	[14, 30]
a (AF)	2.996	2.987	\AA	[14, 30]
$\Delta S_T(T_c)$	11.9	12–14	$\text{J kg}^{-1} \text{K}^{-1}$	[21, 65, 85, 86, 12]
ΔS		17–19	$\text{J kg}^{-1} \text{K}^{-1}$	[40, 22, 30]
$-\Delta T_S$	13	10–13	K	[21, 65]
T_c (AF–FM)	346	353	K	[29]

Table 1: Calculated (Theory) and experimental (Expt.) magnetization, lattice constant, caloric effect, and phase transition temperature. References are given for experiment. ΔS differs from $\Delta S_T(T_c)$ due to incorrect assessment, [30, 40] see sections 3.5 and 5.

transition from an antiferromagnetic (AFM) to a ferromagnetic (FM) state at the critical temperature T_c of 353 K, with a 1% decrease in density [14]. Properties of FeRh were extensively studied experimentally [12, 13, 14, 19, 20, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 21, 43, 44, 45, 46] and theoretically [22, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61]. Notably, the metamagnetic T_c of FeRh is sensitive to stoichiometry, lowering precipitously with small additions of at.%Rh [29]. A giant caloric effect is found at this transition in the quenched $\text{Fe}_{49}\text{Rh}_{51}$ sample [19], i.e., a directly measured temperature drop of 12.9 K at 1.95 Tesla.

While bulk FeRh is prohibitively expensive, Fe–Rh may find use in caloric thin-film [19, 21, 36, 44, 62, 63, 64, 65, 66, 67, 68, 69, 70] and nanoscale devices [43, 59, 71, 72, 73, 74, 75, 76, 77, 78, 79]. Nonetheless, and notably here, it mainly serves as a well-studied but suitably complex system to test methods for reliability in thermodynamic assessments and prediction of caloric properties, specifically because it exhibits instabilities from anharmonic atomic motion, which affects caloric behavior. The FeRh groundstate and a martensitic transformation in the AFM phase at cryogenic temperatures were recently addressed [80].

Here we focus on estimators [8] to predict thermodynamics at the metamagnetic transformation near room temperature. We find that quantities relevant to calorics can be calculated in a quantitative agreement with measurements (Table 1). We also provide insight into the key requirements to predict caloric behavior accurately – necessary to identify the computational screening measures and correlations that assist in materials discovery [81]. While some computations can be intensive (e.g., phonons and lattice entropy), the results are useful for testing faster estimators [82, 83, 84].

Computational details are provided in section 2. In section 3, we address the caloric effects and calculate ΔS_T and ΔT_S at the metamagnetic transition. Importantly, in subsection 3.4 we test a method for addressing non-harmonic atomic vibrations at a relevant temperature, because the commonly-used linear-response and small-displacement methods employed to assess lattice entropy fail near lattice instabilities, including those that arise from anharmonicity of the atomic potential energy surface. In section 4, we offer estimators of enthalpy change ΔH , transition temperature T_c , and its derivative dT_c/dB with respect to the external field B . Some of the issues and limitations of the common and alternative approaches are discussed in section 5. Generic remarks about the upper bounds, chemical disorder, and hysteresis are provided in section 6, with a summary in section 8. Thus, we review and assess the relevant methods and estimates of caloric properties, as showcased in a test system (FeRh), but which may be applied quite generally.

2. Computational methods

For FeRh compound, density functional theory (DFT) calculations were performed using the Vienna *ab initio* simulation package (VASP) [87, 88]. We used projector augmented waves (PAW) [89, 90] and the PBE exchange-correlation functional [91] with Vosko-Wilk-Nusair spin-polarization [92], combined with a modified Broyden method [93] for accelerated convergence. Brillouin zone integrations were performed on a Monkhorst-Pack mesh [94] with ≥ 50 k -points per \AA^{-3} with Γ included. The plane-wave basis-set energy cutoff was increased to 334.9 eV (or 511.4 eV for augmentation charges) by the high-precision flag. During computing of the atomic forces, an additional (third) support grid was used for the evaluation of the augmentation charges.

In non-stoichiometric cases, chemical disorder was addressed using either supercells or the coherent potential approximation (CPA) [95], implemented in the KKR code MECCA [96]. Components of the TTK toolkit [97] were used to prepare the supercells.

As needed for barriers or saddle-point transitions [80], DFT was combined with a generalized solid-state nudged elastic band (GSS-NEB) [98], which includes a built-in C2NEB algorithm [99] with two climbing images [100].

Phonons were calculated using the finite atomic displacement method, implemented in the Phon code [101]. The force-constant matrix [101] was constructed from the atomic forces (in the file FORCES), computed using VASP. The atomic displacements varied from 0.04 to 0.12 \AA in a cubic $4 \times 4 \times 4$ supercell containing

64 FeRh formula units (f.u.). The phonon density of states was computed [101] using 21^3 k -point grid in the reciprocal space (LRECIP=.TRUE.) and the Gaussian smearing (DOSSMEAR=0.05 THz); the output file THERMO provided the lattice entropy S_L at finite T . We used the experimental atomic masses: $m(\text{Fe}) = 55.845$ and $m(\text{Rh}) = 102.9055$ atomic unified mass units, $u = \frac{1}{12}m(^{12}\text{C})$. We also present a method that more properly addresses anharmonic vibration near instabilities, which has a significant affect on entropy.

3. Results

The magnetostructural transition in B2 FeRh between FM and AFM phases (Fig. 1) is accompanied by a change of electronic structure (Fig. 2), energy and volume (Fig. 3). While an electronic transition happens with the speed of light, a structural transformation (including volume change) propagates no faster than the speed of sound [102]. So, the electronic transformation is accompanied by discontinuity in pressure that drives the volume change [103]. The possible causes for electronic transitions include initial structure change or application of an external field. In particular, as is well established, the magnetostructural transformation of FeRh can be caused by application of an external magnetic field and/or stress, strain, or thermal expansion.

3.1. Spin Density and Itinerant Magnetism

Figure 1 shows the real-space distribution of the electronic spin density in the B2 cubic cell of FeRh, which is an itinerant magnet. Importantly, spin density around Rh atoms is not zero in both phases, but the atomic magnetic moment of Rh is zero in an ideal B2 AFM structure due to the inversion symmetry with a center at Rh nucleus. Indeed, if the distribution of Fe moments is symmetric in the AFM phase, then the electronic spin density sums to zero within the Rh atomic sphere (and within an arbitrary Rh-centered sphere of any radius). However, any asymmetry due to the fluctuating Fe-Rh distances or Fe moments (e.g., due to thermal disorder) would result in a non-zero atomic magnetic moment of Rh.

At the AFM-FM phase transition, the calculated magnetization changes from zero to $149 \text{ A m}^2/\text{kg}$ ($4.2 \mu_B/\text{FeRh}$). With caution, one can integrate the spin density inside each atomic sphere to find the “atomic” magnetic moment. We find that the Rh moments change from 0 (AFM) to $1 \mu_B$ (FM), and the Fe moments change from ± 3.1 (AFM) to $3.2 \mu_B$ (FM).

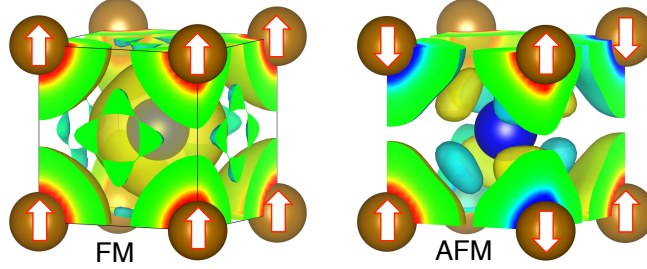


Figure 1: (Color online). In B2 FeRh, the electronic spin density as $\pm 0.002 e/\text{\AA}$ isosurfaces in (001) FM (left) and (111) AFM (right) spin configurations.

3.2. Electronic and Magnetic Entropy

As seen in Fig. 2, the total electronic spin density of states (DOS) at the Fermi energy E_F changes substantially during the transformation from $n(E_F) = 0.677$ in the AFM to 2.310 states/eV per FeRh formula unit (f.u.) in the FM state. Contributions of both spins are equal in the AFM, while minority spins dominate at E_F in the FM state (Fig. 2).

The electronic entropy (as estimated by the Sommerfeld's expansion) is

$$S_e(T) \approx (\pi^2/3) \cdot k_B^2 T \cdot n(E_F), \quad (1)$$

which yields 0.23 (FM) and 0.07 (AFM) k_B/FeRh at T_c . The difference ΔS_e is $0.163 k_B/\text{FeRh}$ (or $0.08 k_B$ per atom). The Sommerfeld approximation in most cases tested has been a reasonably reliable approximation between structural variants arising at solid-solid phase transitions.

Spin-polarized electrons are responsible for both conductivity and magnetism; they account for both electronic and magnetic contributions to the entropy, as required in an itinerant magnet [82], such as FeRh. Fluctuations of atomic magnetic moments can be expanded in an electronic basis in both FM and AFM phases. S_e includes entropy of thermal excitations in both spin channels (i.e., electronic and magnetic contributions).

The total entropy is $S = \ln \Omega$, where Ω is the number of accessible microstates in the whole system. Typically, magnetic entropy is small in the FM and AFM states, where the number of magnetic states (per atom) is close to 1, and it is larger in a paramagnetic (PM) state, which is not relevant to the AFM–FM phase transition. In decomposing the total entropy into electronic, magnetic, and lattice contributions, sometimes mistakes were made [40], leading to notably wrong

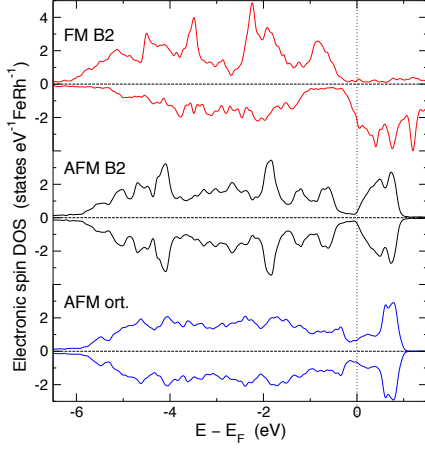


Figure 2: (Color online). For B2 FeRh, electronic DOS for FM (upper) and AFM spin ordering in ideal cube, and AFM orthorhombic structure (lower) at zero pressure [61].

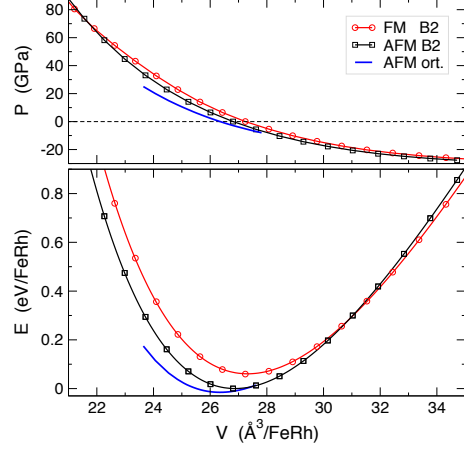


Figure 3: (Color online). Pressure P (GPa) and energy E (eV) vs. volume V (\AA^3 per FeRh formula unit for B2 FM and AFM, and orthorhombic AFM structures).

findings.¹ We discuss the issues with indirect assessments in section 5.

3.3. Compression and Expansion

The energy E and pressure P versus volume V curves for the main competing structures in FeRh are shown in Fig. 3. The FM B2 and AFM B2 are the terminal states of the metamagnetic phase transition, accompanied by the magnetocaloric effect; the AFM orthorhombic (martensitic) ground state of FeRh is discussed elsewhere [80]. The calculated equilibrium lattice constants $a = V^{1/3}$ are compared to experiment in Table 1, less than +0.2% difference from experiment using a PBE density functional. The FM and AFM states have a crossover at higher volumes. From these plots, the metamagnetic transition already can be anticipated. At zero pressure P , the FM state is $\delta H_0 = 29.8 \pm 1.0$ meV/atom above the AFM state ($\delta H_0/k_B = 346 \pm 12$ K, i.e., near the measured $T_c = 353$ K, see section 4).

In addition, a premartensitic instability is anticipated in B2 AFM state with known phonon instabilities [57, 58, 59], and a martensitic transformation from B2 AFM austenite to orthorhombic AFM martensite at cryogenic T was suggested by direct GSS-NEB calculations [61].

¹ In Ref. [40], the total integrated entropy difference ($\Delta S = 17 \pm 3$ J/kg/K) was incorrectly decomposed into lattice ($\Delta S_{\text{latt}} = -33 \pm 9$ J/kg/K), electronic ($\Delta S_{\text{el}} = 8 \pm 1$ J/kg/K), and magnetic ($\Delta S_{\text{mag}} = 43 \pm 9$ J/kg/K) contributions. The negative sign of the lattice contribution is notable.

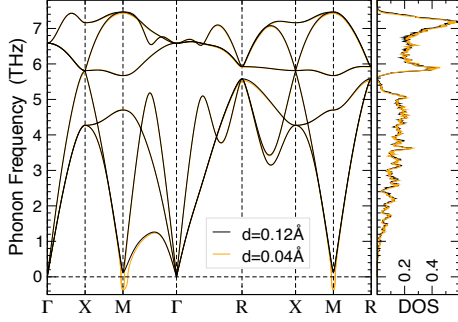


Figure 4: (Color online). Phonon frequencies and DOS for AFM B2-FeRh (2.996 Å) using small (0.04 Å) and large (0.12 Å) displacements. Unstable phonons at M ($\frac{1}{2}\frac{1}{2}0$) appear at $d \leq 0.06$ Å.

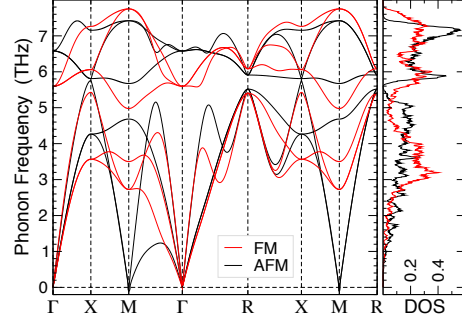


Figure 5: (Color online). Phonon frequencies and DOS for FM and AFM states in B2-FeRh (2.996 Å) evaluated with $d(\text{Fe}) \approx d(\text{Rh}) \approx 0.06$ Å at $\frac{1}{2}k_B T_c$, see text and Fig. 6, now no unstable phonons at M ($\frac{1}{2}\frac{1}{2}0$).

3.4. Lattice Entropy – Anharmonic and Harmonic Vibrations

Vibrational entropy in materials can contribute significantly to their caloric response. To assess vibrational entropy of phonon excitations at a finite T , the standard approach is to calculate the quasiharmonic phonon frequencies by linear-response or small atomic displacement method. However, both of these methods inherently assume a harmonic atomic potential. In materials with structural and magnetic instabilities (or, more generally, “dimpled” potential energy surfaces), this assumption is invalid, at least near temperatures, where the crossover between states occur and key associated properties manifest. With the premartensitic instability [80] in AFM(111) B2 FeRh, similar (but smaller) to that in NiTi austenite [16, 17], care must be taken to calculate accurately the lattice entropy.

Here, distinct from previous work, we evaluate phonon frequencies and density of states (DOS) along with their sensitivity to the atomic displacement d used to calculate them. Using the small-displacement method [101] at zero pressure, we find an unstable phonon mode at M ($\frac{1}{2}\frac{1}{2}0$) in the AFM state (Fig. 4), but not in the FM state (Fig. 5), as also found in recent publications [58, 59, 60]. At ambient conditions, FM FeRh is stable but not harmonic, with instabilities nearby (e.g., due to strain) [58]. For the least harmonic phonons, frequency dependence on d is the strongest. The high-frequency optical phonon modes are harmonic in FM and AFM phases, while the low-frequency acoustic phonons show less harmonic behavior around M , where the difference between modes, calculated for $d = 0.04$ and 0.12 Å, is the largest (Fig. 4).

Notably, the M-point phonon instability leads to a cryogenic martensitic tran-

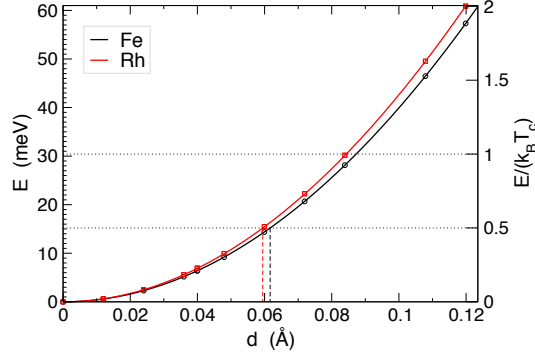


Figure 6: (Color online). For FM B2 FeRh (2.997 Å), energy (E , meV) versus displacement d of a Fe (black) or Rh atom (red) along [100] compared to $k_B T_c$. Lines are quartic fits.

sition in AFM FeRh with atomic shuffles of $d_{Fe} = 0.061$ and $d_{Rh} = 0.053$ in fractional lattice coordinates, showing that atomic potentials have dimples around the high-temperature symmetric structure (B2) and are inherently anharmonic. [61] One anticipates then a d -dependence of phonon frequencies, which are well-defined at each fixed d .

To calculate phonons at a given temperature T , one could use thermal atomic displacements and forces from *ab initio* molecular dynamics (MD), say, in the ThermoPhonon code [16, 104]. A faster, albeit more approximate, method (which we use at T_c of 353 K) is an application of the quasiharmonic approximation with a finite single-atom displacement d scaled to a “thermal” potential energy $E(d) = \frac{1}{2}k_B T$ in an ideal structure (Fig. 6). This method is applied to FeRh in Fig. 5 and shows that AFM B2 structure has an unstable phonon mode at M with an amplitude of only 0.1 i THz (i.e., close to zero) at “thermal” displacements $d(T_c) \approx 0.06$ Å [here $d(Fe) \neq d(Rh)$, see Fig. 6]; this instability becomes larger at smaller d (including infinitesimal case used in linear-response methods) and disappears at larger d .

As phonons in both AFM and FM phases are anharmonic, and the lattice entropy S_L is affected mostly by the soft phonon modes, this finite-displacement method within a quasiharmonic approximation [105] is a reliable computational “trick” to avoid unstable phonons at a relevant finite temperature; it uses substantially less computational time than the other method based on MD at fixed T [16], while yielding correct estimates.

The atomic displacement $d(T)$ can be adjusted to temperature T (Fig. 6) and used to evaluate the T -dependent lattice entropy $S_L[T, d(T)]$, calculated at fixed

lattice constants. Below we use the phonon DOS to evaluate ΔS_L at the metamagnetic transition at T_c (Fig. 7). Importantly, due to anharmonicity and finite thermal displacements at finite temperature, $\Delta S_L[T_c, d(T_c)]$ is increased by 50%, compared to $\Delta S_L[T_c, d \rightarrow 0]$.

In particular, for FM B2 FeRh, the energy E versus atomic displacement d (shown in Fig. 6) can be fit well by a quartic (not quadratic) polynomial, i.e., $E(d) = E^{(2)}d^2 + E^{(4)}d^4$. We find $E_{Fe}^{(2)} = 4.003 \text{ eV/\AA}^2$ and $E_{Fe}^{(4)} = -1.030 \text{ eV/\AA}^4$ for Fe and $E_{Rh}^{(2)} = 4.317 \text{ eV/\AA}^2$ and $E_{Rh}^{(4)} = -5.496 \text{ eV/\AA}^4$ for Rh. Consequently, S_L depends on the atomic displacement d , see Fig. 8. In the FM phase, it changes from $8.859 k_B/\text{FeRh}$ for small $d = 0.04 \text{ \AA}$ to $8.972 k_B/\text{FeRh}$ for large $d = 0.12 \text{ \AA}$ at fixed $a = 2.997 \text{ \AA}$. In the AFM phase, we find a small change from 8.8176 to $8.7945 k_B/\text{FeRh}$ for the same fixed values of d , see Fig. 8. Interestingly, the unstable AFM B2 phase is less anharmonic than the stable FM B2 phase, which develops phonon instability at a strain [58]. The small- d (0.04 \AA) method provides ΔS_L of $0.042 k_B/\text{FeRh}$ (or $0.02 k_B$ per atom). However, with T -dependent displacements $d(T_c) \approx 0.06 \text{ \AA}$ ($d_{Fe} \neq d_{Rh}$, see Fig. 6), $\Delta S_L[T_c, d(T_c)]$ increases by 50% to $0.064 k_B/\text{FeRh}$ (or $0.03 k_B$ per atom), see Fig. 7. Thus, for FeRh, the spin-polarized electrons, fully accounted here, provide the leading contribution to the total entropy change $\Delta S_T(T_c)$, while the lattice entropy contribution is smaller (only 28%), but not negligible. This relative contribution agrees with an early prediction [22] and its recent confirmation [53]. Nonetheless, for FeRh, $\Delta S_L(T_c)$, now increased by 50% from anharmonicity, is $\approx 40\%$ of the calculated electronic contribution $\Delta S_e(T_c) = 0.163 k_B/\text{FeRh}$.

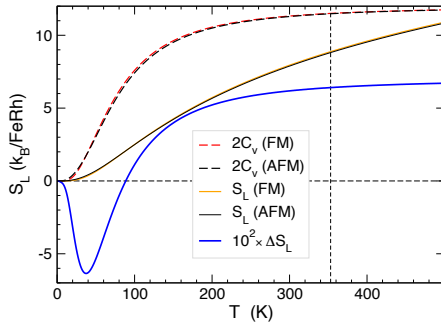


Figure 7: (Color online). For B2 FeRh, heat capacity C_V , S_L , and $\Delta S_L(\text{FM} - \text{AFM})$ from phonons (Fig. 5) using $d(T_c) \approx 0.06 \text{ \AA}$ from Fig. 6. T_c at 353 K is denoted by vertical dashed line.

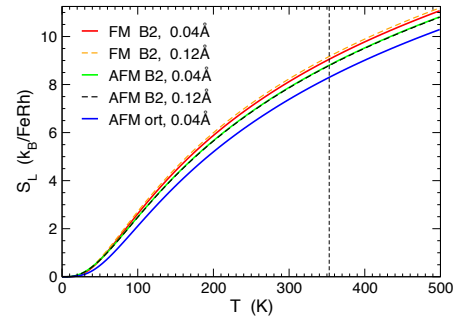


Figure 8: (Color online). For B2 and orthorhombic FeRh structures in FM and AFM states at $P=0$, lattice entropy S_L using small (0.04 \AA) and large (0.12 \AA) atomic displacements d .

Anharmonicity affects the phonons and associated thermodynamic quantities. In general, anharmonic effects must be properly included in a consideration of thermodynamics near lattice instabilities and phase transitions. Here, we have described a quick method to include these T -dependent effects in anharmonic systems by probing the amplitude of atomic displacements d dependence of the vibrational frequencies. If the phonons were harmonic, then the lattice entropy $S_L[T, d(T)]$ would not depend on d [101, 105]; Fig. 8 shows that in FeRh this is not the case, as d in the FM B2 state is larger than for the AFM state.

3.5. Entropy Change

The total entropy includes the electronic (with magnetic) and lattice contributions. We calculate the total entropy change $\Delta S = S(\text{FM}) - S(\text{AFM})$ due to electronic transformation at $T_c = 353$ K at fixed lattice constant $a = 2.997$ Å (measured [14] in the Fe₅₀Rh₅₀ FM phase at T_c). We find $\Delta S_T = 0.227 k_B/\text{FeRh}$, or $0.11 k_B/\text{atom}$ (i.e., $11.9 \text{ J kg}^{-1} \text{ K}^{-1}$) for the isothermal total entropy change at the metamagnetic transformation at T_c at fixed volume. The lattice entropy contribution ΔS_L is 28% of ΔS_T ; ignoring the anharmonic effects would lead to a 50% relative error in ΔS_L and 14% error in ΔS_T .

In experiment, the maximum total entropy change of $12.5 \pm 1 \text{ J kg}^{-1} \text{ K}^{-1}$ was the same for both baro- and magneto-caloric effects in Fe₄₉Rh₅₁ [65]. Three assessment methods gave comparable values for ΔS_T for the Fe₄₉Rh₅₁ [21], namely, calorimetry: 12.1, Clausius-Clapeyron: 13.1, and Maxwell relations: $13.6 \text{ J kg}^{-1} \text{ K}^{-1}$. An earlier measurement [12] yielded $14.0 \text{ J kg}^{-1} \text{ K}^{-1}$ for stoichiometric FeRh and found a compositional dependence of ΔS for the samples doped with Pd, Pt, or Ir. The experimental values [in $\text{J} \cdot \text{kg}^{-1} \text{ K}^{-1}$] for ΔS_T of 13.6 [21], 12.5 ± 1 [65], 13 ± 1 [85], 13 ± 1 [86], and 14 [12] differ from the higher assessed values of 19 ± 2 [30], 18.3 [22], and $17 \pm 3 \text{ J kg}^{-1} \text{ K}^{-1}$ [40]; inaccuracies in Refs. [30, 22, 40] originated from subtracting values measured at two different compositions [40], using [30] ΔV_P instead of ΔV_T in the Clausius-Clapeyron equation (7), see section 5, or increasing the extrapolated value of $(dB_c/dT)_{B=0}$ in eq. 6 to account for an overestimated magnetocaloric effect in a Fe_{0.48}Rh_{0.52} sample [22]. The assessed values depend on the method [21], sample composition [12], and preparation [19]. The calculated and experimental values are compared in Table 1.

3.6. The Caloric Effect

The maximum isentropic temperature change is

$$\Delta T_S = -T_c \Delta S_T / C_B. \quad (2)$$

Here $C_B(B, T)$ is the heat capacity at constant magnetic field B . Using the asymptotic limit $C_B \approx 3k_B/\text{atom}$ ($6k_B/\text{FeRh}$ or $314 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$) for solid FeRh at $T \geq 300 \text{ K}$ (Fig. 7) and our value of ΔS_T (section 3.5), we find $\Delta T_S = -13 \text{ K}$. This value agrees with the experimental assessments [21], ranging from -10.6 to -12 K , see Table 1. However, it differs from an early estimate [22] of $\Delta T_S = -(20 \pm 2) \text{ K}$, obtained using too high value of $\Delta S = 18.3 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ in eq. 2. The directly measured adiabatic temperature change $\Delta T_{ad}(\Delta B)$, produced by an added external field of $\Delta B = 1.95 \text{ Tesla}$, can be as large as -12.9 K for the quenched $\text{Fe}_{49}\text{Rh}_{51}$ samples [19].

4. Estimators for Materials Screening

Isothermal enthalpy change $\Delta H_T(T_c)$

From Gibbs relation, the isothermal enthalpy change ΔH_T at T_c is the key quantity, given by the formally exact equation

$$\Delta H_T(T_c) = T_c \cdot \Delta S_T(T_c). \quad (3)$$

Using either experimental or calculated (below) T_c and calculated $\Delta S_T(T_c) = 11.9 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$, we get $\Delta H_T(T_c) = 4.2 \text{ kJ/kg}$ or 6.9 meV/FeRh . In general, $\Delta H_T \neq \Delta H_P$, but ΔH_P is typically measured in experiments at fixed external pressure P .

Transition Temperature T_c

We note that transition temperature T_c in eq. 3 can be estimated accurately in mean-field approximations but only if considered separately for segregating (immiscible) [106] and ordering (miscible) systems [107], which have a negative formation enthalpy, e.g., stable solid-solution phase.

For a segregating system, a mean-field approximation was shown to be highly accurate for miscibility gaps (the so-called T_0 line) away from compositional limits (i.e., $c_\alpha \rightarrow 0$ or $c_\alpha \rightarrow 1$ for an α atomic type), where mean-field entropy differences are less accurate. (Careful Monte Carlo simulations were used to confirm the accuracy [106].) However, in these cases, vibrational entropy changes can have a large effect in T_c , where analytically it is changed when going between two phases (e.g., solid solution and segregation) as

$$T_c = T_{c,conf} \left(1 + \frac{\Delta S_L}{\Delta S_{conf}} \right)^{-1}, \quad (4)$$

where the subscript “conf” delineates the configurational entropy only and ΔS_L is the lattice vibrations entropy changes. Moreover, to a good approximation (at least in binary metals), [108, 109] the lattice vibrational change $\Delta S_L \approx -0.34\Delta\chi$, where $\Delta\chi$ is the electronegativity difference between alloying pairs. So, if the electronegativities of elemental pairs are similar, there is no effect from vibrations on T_c and estimates without vibrational calculations are fine, as discussed in Ref. [106]. Otherwise, changes in vibrational entropy can be estimated at a given temperature, as we have outlined earlier.

Typically, the sign of a formation enthalpy H_f indicates either segregation ($H_f > 0$) or ordering ($H_f \leq 0$) tendency. Any diffusion broadens the hysteresis, while a chemical inhomogeneity smears a diffusionless phase transition; both effects are consequences of a segregation tendency, which should be avoided in caloric materials. Fortunately, a positive formation enthalpy can easily be monitored during materials screening.

In contrast to segregation for miscible alloys (e.g., FeRh systems exemplified here), a T_c estimate for a first-order transition between two phases can be estimated well by

$$T_c = I_c \cdot \delta H_0 / k_B, \quad (5)$$

where δH_0 is the enthalpy difference between fully-relaxed structures at zero temperature, and $I_c \sim 1$ (dimensionless) is a factor with a constant value for a class of similar systems. Please keep in mind that δH_0 should not be confused with $\Delta H_T(T_c)$, and, as expected, $\Delta H_T(T_c) \ll \delta H_0(0\text{K})$, as numerically exemplified before [110]. We have found that eq. 5 accurately estimates order-disorder transitions in metallic alloys [111, 112] and martensitic phase transitions [16, 17, 107].

Equation 5 with $I_c = 1$ is exact for barrierless transitions, whereas generally I_c is proportional to a ratio (of functions of order parameters) nearing 1 between the two systems, such as two magnetic configurations in a fixed chemical cell or in an order-disorder transitions in a fixed magnetic state [107]. For example, the calculated enthalpy difference δH_0 between AFM and FM B2-FeRh is 29.8 ± 1 meV/atom (Fig. 3); this value compares well with previous calculations [49]. For the metamagnetic phase transition in FeRh, we find that $(\delta H_0 / k_B) = 346 \pm 12$ K, which compares well with $T_c = 353 \pm 1$ K measured in Fe₅₀Rh₅₀ [29]. The value of I_c near 1 has uncertainty due to an error in DFT energies and in the measured T_c . As the chemical structure is fixed for FeRh metamagnetic transition and only the magnetic configuration changed, it is purely an electronic configurational change.

Equations 3 and 5 are exact, while $I_c \approx 1$ is approximate. For barrierless transitions, the enthalpy difference δH_0 coincides with the energy needed to excite an

additional degree of freedom (DoF) and access the higher-temperature phase, and in the classical limit $I_c \equiv 1$ in this case. This interpretation of eq. 5 was successfully applied to estimate melting temperatures [113]. The apparent simplicity of the estimate (5) obscures a complicated counting of the number of the effective DoF [113]. In general, a higher- T phase has more DoF contributing and consequently a higher entropy than the lower- T phase. The change in the number of effective DoF is an integer, hence, a reasonable accuracy of the eq. (5) with $I_c \approx 1$ is not a coincidence. As both atomic and spin orderings can be described by a basis-set expansion [97], a similar equation for different physics is obtained. One can assess eq. 5 for generic alloy screening, as exemplified for order-disorder transitions in Table 2 or for solid-solid phase transitions in Table 3.

System	GS	δH_0 (meV)	$k_B T_c$ (meV)	T_c (K)	Expt. (K)	I_c^{-1}	Ref.
Ag ₃ Al	(D0 ₂₂)	46	45	520	-	0.98	[114, 115, 116]
Ag ₂ Al	(MoPt ₂)	41	37	430	-	0.91	[114, 115, 116]
AgAu	[L1 ₀]	12.2	14	165	-	1.13	[117]
AgAu	[L1 ₀]	16.7	-	-	-	-	[118]
CuAu	L1 ₀	47	48.3	560	658	1.03	[119]
Cu ₃ Au	[L1 ₂]	42.8	-	-	500	-	[118]
Ni ₃ V	D0 ₂₂	115	118	1370	1318	1.03	[97]

Table 2: Calculated order-disorder enthalpies δH_0 (meV/atom) and $k_B T_c$ (meV) and T_c (K) for some fcc (miscible) binaries, using our data from Table 3.4 in Ref. [110]. Strukturbericht designations in brackets [...] are assumed ground states structures; structures in parenthesis (...) are metastable. Calculated T_c 's were obtained from Monte Carlo using a cluster expansion, and compared to experimental (Expt.) values [120, 121].

Compositional Sensitivity of T_c

Notably, T_c scales with δH_0 in both stoichiometric (50 at.% Rh) and off-stoichiometric alloys with a partial atomic disorder, including with long-range order parameter, see, e.g., Ref. [107]. From the electronic density of states (DOS) $n(E)$ in Fig. 2, also seen in recent calculations [57, 58, 59], we expect that lowering of the Fermi energy E_F (due to decrease in Rh fraction) will stabilize the FM phase (from a lower DOS in the pseudogap), but it would have a lesser effect on the AFM phase. This change will decrease δH_0 and will reduce T_c . Indeed, this qualitative expectation agrees with the experimental phase diagram [29, 37, 124]. Compositional hypersensitivity of FeRh was theoretically studied in Ref. [53].

System	Phase	Transition	δH_0 (meV)	$\delta H_0/k_B$ (K)	T_c (K)	I_c^{-1}	Ref.
Ti	hcp	hcp-bcc	97.2	1128	1155	0.976	present
Hf	hcp	hcp-bcc	174.2	2022	2016	1.003	present
NiTi	bco	martensitic	29.5	343	333	1.030	[17]
FePd	$L1_0$	FM-PM	64.5	749	730	1.026	[122]
FePt	$L1_0$	FM-PM	63.3	735	750	0.980	[122]
CoPt	$L1_0$	FM-PM	59.6	692	720	0.961	[122]
MnNiSi	$Pnma$	FM-PM	55.7	646	662	0.976	present
LiBH ₄	$Pnma$	melting	45.3	526	553	0.951	[113]
FeRh	B2	AFM-FM	29.8	346	353	0.980	present

Table 3: Calculated examples of relative enthalpies δH_0 (meV/atom) between low-T and high-T phases are compared to experimental T_c 's [121, 123], with $I_c^{-1} = \delta H_0/k_B T_c$ (dimensionless).

Field Dependence of T_c

Dependence of T_c on the external magnetic field B , as well as dependence of the critical field B_c on T , assuming $(dB_c/dT)^{-1} = dT_c/dB$, can be determined from discontinuities in magnetization M and entropy S at the first-order meta-magnetic transition:

$$\frac{dT_c}{dB} = \frac{\Delta M_{T=T_c}}{\Delta S_{T=T_c}}. \quad (6)$$

The calculated magnetizations of the fully-relaxed B2-FeRh in AFM and FM states are 0 and $2.1 \mu_B/\text{atom}$, respectively (Section 3.1). For the upper bound $\Delta M(T_c) < [M(\text{FM}) - M(\text{AFM})]$ for the magnetization change at T_c , we find $\Delta M/\Delta S_T < 2.1 \mu_B/0.103 k_B = 13.7 \text{ K/Tesla}$. However, a more realistic value [42] of $(\Delta M)_{T_c} - 60\%$ of the upper bound – gives $-dT_c/dB = 8.2 \text{ K/Tesla}$ for stoichiometric FeRh. Measurements of $T_c(B)$ in the external magnetic field (or critical field vs. T) provide a quadratic [34] dependence with the linear [30] slope $-dT_c/dB$ in small fields of 8.2 in FeRh [12]; 8.2 in Fe_{49.5}Rh_{50.5} [42]; 8.5 in Fe₄₉Rh₅₁ [21]; and from 9.6 to 9.7 K/Tesla in Fe₄₉Rh₅₁ [65].

Accuracy

As shown, a number of standard approximations within DFT calculations work very well for estimating many thermodynamic quantities, in particular for caloric properties, such as transition temperatures T_c , field-dependent changes in T_c , and electronic entropy changes ΔS_e (the main contribution), while the significant lattice entropy changes ΔS_L are underestimated for anharmonic atomic

vibrations, which are found in many systems with lattice instabilities. However, we established a direct method to evaluate more correctly ΔS_L , which gave a 50% increase in its magnitude, and provided more accurate estimates of caloric properties, see Table 1. It remains to test these estimators in more complex systems to screen for improved caloric materials via an approach presented recently [8].

5. Issues with Indirect Assessments

Before closing, we would be remiss not to remark on quantities that are difficult to assess theoretically due to errors or inability to measure experimentally, clearly relevant to materials screening, and occasional incorrectly applied.

Often the measured dT_c/dP and ΔV is used to evaluate ΔS using the Clausius-Clapeyron equation

$$\frac{dT_c}{dP} = \frac{\Delta V_T}{\Delta S_P}. \quad (7)$$

However, there is a well-known problem with applications of this equation to experimental data [125]. Specifically, while it is possible to measure pressure P and the corresponding volume change (ΔV_P) at a first-order transition, the isothermal volume change (ΔV_T) induced by varying P is not measured; and, furthermore, there is no reason that ΔV_T and ΔV_P are the same. Nonetheless, there have been instances where ΔV_P was used as equal to ΔV_T to use eq. 7, which gives an overestimate of ΔS , see, for example, Ref. [30]. Such disagreements of estimates from eq. 7 and direct measurements are well documented [125]. Pressure dependence of T_c has been long discussed [30, 125, 126]; the measurements [126] of dT_c/dP in FeRh range from 43 [30] to 64 K/GPa [65].

Regarding the accuracy of DFT-calculated energy (E) versus volume (V) curves (Fig. 3), the lattice constants a_0 (at $P = 0$ GPa, $T = 0$ K) are 2.996 Å in AFM and 3.012 Å in FM phase for B2 FeRh, while the measurements on Fe₅₀Rh₅₀ at 353 K give 2.987 Å and 2.997 Å, [14] similar to results in Ref. [30], see our Table 1. So, with calculated lattice constants having a relative error of $\pm 0.3\%$, the calculated volume $V \sim a^3$ has an error of $\pm 1.2\%$, too large to determine reliably a change of $\Delta V/V \approx 1\%$, as found relevant in experiment [14]. So, one cannot use the Clausius-Clapeyron relation to assess dT_c/dP , if looking for outliers for desired caloric properties.

Magnetic entropy S_M is typically assessed by thermodynamic integration using experimental data:

$$\Delta S_M(T, \Delta H) = \int_{H_1}^{H_2} dH \frac{\partial M(T, H)}{\partial T} \Big|_H. \quad (8)$$

Importantly, this equation is valid within a single phase. Derivative $\partial M/\partial T$ diverges at the metamagnetic first-order phase transition. Thermodynamic integration should not be performed across phase boundaries.

In addition, the difference between values in two phases should be calculated by subtracting values obtained for the same chemical composition, otherwise improper or misleading results can be derived, as in Ref. [40], where two epitaxial Fe-Rh films of different compositions we used, i.e., Fe-rich with FM ground state and Rh-rich with AFM ground state.

6. Generic Remarks

6.1. Bounds and Dominant Contributions for Entropy Change

For any type of screening, it is useful to note the largest contributions that can be expected to control desired behavior. For caloric behavior, electronic and lattice entropy changes due to electronic- or structural-driven instabilities are most critical and we can approximate the largest possible values. Namely, for d -band (f -band) systems, the electronic spin (magnetic) entropy changes $\Delta S_e \leq \Delta S_e^{max}$ have upper limit of $\Delta S_e^{max}/k_B = \ln(2^{n/2})$ of 3.47 (4.85) per half-filled band with n being 10 d (14 f) orbitals; this is essentially the maximum permitted magnetic entropy change from atomic magnetization. ΔS_e cannot be larger than the electronic entropy S_e of either phase, as estimated by eq. 1. A phase transition accompanied by a large change of electrical conductivity (proportional to electronic DOS at E_F , i.e., $n(E_F)$) is expected to have a good ΔS_e .

If the transition temperature between competing states is above the respective Debye temperatures, the vibrational entropy change for a solid-solid transition is approximated by

$$\Delta S_L \approx 3k_B \ln(\Theta_2^D/\Theta_1^D), \quad (9)$$

where Θ_α^D is the Debye temperature of the phase α . For Θ_2^D/Θ_1^D of 1.0 to 1.5, a safe upper-bound range for solids of the same stoichiometry and pressure, we get $0 \leq \Delta S_L < 1.22k_B/\text{atom}$ for quasiharmonic solids, a bound smaller than that for electronic contributions (i.e., $\Delta S_L < \Delta S_e$). Also, ΔS_L in a solid with non-harmonic phonons can be larger than that in a harmonic solid, as already demonstrated. The general expectation then is that the combined electronic and magnetic entropy changes will constitute the dominant contributions to the total ΔS_T for caloric systems, while the lattice entropy can be significant but secondary (and more demanding to estimate reliably). An estimate of the dominant effect (and its bounds) is used for the high-throughput pre-screening of materials [81, 8].

6.2. Chemical Disorder and Segregation

Caloric material is expected to have a phase transition at the target temperature T . However, stoichiometric line compounds typically have off-target values of T_c . To correct this, chemical composition is altered and an off-stoichiometric chemical disorder is introduced. For a large caloric effect, the first-order phase transition must be sharp, and consequently the caloric material must be chemically homogeneous. Any segregation will be detrimental to such homogeneity.

To screen out segregating materials, we use the coherent-potential approximation (CPA), [95] implemented in the KKR electronic-structure code, [96] to compute dependences of the formation enthalpy H_f on composition c , considering possible disorder on each sublattice. (One can also use large representative supercells at a number of discrete compositions, but, if done carefully, those results usually compare well with the output of KKR-CPA, which is much faster to compute due to smaller cells with fewer atoms and electrons.) If immiscible, i.e., $\partial^2 H_f / \partial c^2 < 0$, then $H_f(c)$ is concave and the system can lower its energy by developing a compositional inhomogeneity (segregation) that is unfavorable for calorics. Such materials are rejected, such as $(\text{Hf}_{1-c}\text{Nb}_c)\text{Fe}_2$ Lave’s phase (Fig. 9 in Ref. [127]). In contrast, a convex $H_f(c)$ (in miscible system with $\partial^2 H_f / \partial c^2 > 0$) is a necessary but not sufficient condition for good caloric properties. An example with a convex $H_f(c)$ is $\text{ZrMn}_6(\text{Sn}_{1-c}\text{Sb}_c)$, see Fig. 8 in Ref. [8].

6.3. Hysteresis

A first-order phase transition is usually accompanied by a hysteresis. The width of the hysteresis serves as huge loss factor for caloric cooling, unless the hysteresis can be eliminated [128]. Nucleation, lattice mismatch, and enthalpy barriers for nucleation and phase boundary propagation contribute to the width of the hysteresis. Fortunately, we know how to reduce the hysteresis width.

Compositional changes affects the lattice constants in each phase. The lattice mismatch between austenite and martensite can be made to go to zero and the hysteresis thereby narrowed by the fine tuning of composition c [129], which occurs when the middle eigenvalue (λ_2) of the transformation stretch tensor attains the value 1 at T_c . While $\lambda_2(c)$ could be monitored versus composition, it is far more convenient and straightforward to assess the dependence of the lattice constants in the relevant phases on composition at fixed (P, T) , as computed in DFT, see section 2. The KKR-CPA permits to do this easily and quickly for materials with disorder, as we have done many times. Typically, only a few calculations are needed to find compositions where lattice match is achieved.

Finally, defects (e.g., surface geometry, bulk impurities, precipitates, or second-phase remnants due to incomplete transformation) can serve as nucleation centers, suppressing the nucleation enthalpy barriers. Design of caloric devices should account for the nucleation centers in caloric materials. The enthalpy barriers for the phase boundary propagation depend on composition. We calculate them using the nudged elastic band (NEB) methods [130, 98, 100]. Unfortunately, T_c depends on composition, too. Hence, reduction of the hysteresis at constant T_c by adjusting c is similar to tuning a piano: several compositional degrees of freedom must be simultaneously or iteratively adjusted to get the target values for both T_c and hysteresis width. Nevertheless, trends can be assessed with relatively few calculations to find better design regions, or eliminate systems quickly [8].

7. Beyond FeRh: Novel Materials with Giant Magnetocaloric Response

Recently, we utilized some of these methods to search among 10,000+ candidates and to reduce systems of interest for our experimental collaborators, eliminating thousands alloys [8]. Out of all systems scanned, about ten (or 0.1%) were found ("predicted") to have caloric behavior either similar to FeRh (i.e., $\Delta S_T \geq 12 \text{ J kg}^{-1} \text{ K}^{-1}$), but lower in cost or significantly improvable with modifications to alloying chemistry. Several classes of these materials are now being investigated experimentally. For example, Ni-Co-Mn-Ti [131] and $\text{Mn}_{0.5}\text{Fe}_{0.5}\text{NiSi}_{1-x}\text{Al}_x$ [132] have been confirmed to be promising for the solid-state refrigeration, with enhancement of ΔS_T well above $20 \text{ J kg}^{-1} \text{ K}^{-1}$ at room temperature. Such discovery will be accelerated when this type of screening is implemented through a database combined with key correlations derived by machine-learning techniques, especially when looking for outliers in desired properties – just as with systems with zero hysteresis at phase transformations, where the desired compositional range may consist of a single point [129].

8. Summary

We have explored several thermodynamic estimates for assessing caloric properties in alloys. We used FeRh as a testbed, as it exhibits large multicaloric (magneto-, elasto- and baro-caloric) responses at its metamagnetic transition just above room temperature, as well as non-harmonic vibrations – typical for systems near lattice instabilities. We showed that use of controlled T -dependent atomic displacements, easily estimated at T_c , provides a reliable assessment of lattice entropy changes at the phase transition. In FeRh, we tested approximate methods

and estimators, and evaluated a number of thermodynamic properties, including specific heat, entropy and enthalpy changes, transition temperature, and isentropic temperature drop. The predicted caloric properties are in a quantitative agreement with the trusted experimental data, see Table 1. We have verified that these estimators are reliable (if applied carefully) and accurate. In contrast, we showed that some previously used assessments, like from the Clausius-Clapeyron relation (7), are unreliable due to the underlying assumptions. Thus, assessment and testing of the methods were a necessity.

Tested reliable methods will enable faster theory-guided screening to find more promising caloric materials, involving more complex multicomponent systems on which to focus. Indeed, the estimates provided here already resulted in finding improved lower-cost caloric systems exhibiting giant magnetocaloric enhancements with promise for use in solid-state cooling [131, 132].

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